Physics of polymer melts: A novel perspective

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Abstract

We have mapped the physics of polymer melts onto a time-dependent Landau-Ginzburg $|\psi|^4$ field theory using techniques of functional integration. Time in the theory is simply a label for the location of a given monomer along the extent of a flexible chain. With this model, one can show that the limit of infinitesimal concentration of a polymer melt corresponds to a *dynamic* critical phenomenon. The transition to the entangled state is also shown to be a critical point. For larger concentrations, when the role of fluctuations is reduced, a mean field approximation is justifiably employed to show the existence of tube-like structures reminiscent of Edwards' model.

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Issues in polymer melt physics have continued to provide an enduring source of theoretical investigations, owing to the complexity of the field. The basic physics of flexible polymer melts is embodied in Flory's theorem[1]. This theorem states that for low densities, fluctuations in the melt are quite pronounced, while for large densities, fluctuations are so suppressed that the polymers behave as independent Gaussian chains again. One purpose of this paper is to modify the current perspective of polymer melt physics in the interesting low density regime. Rather than this state being close to a critical point in the static sense[1], the connectivity of the chains in the system implies that the physics can be mapped onto a dynamic critical phenomenon. In the old picture, global properties such as the radius of gyration R_g (end-to-end distance) were shown to possess scaling properties, while local properties of chains could not be addressed. The new view-point allows a computation of the local structure of individual chains as well. Our estimate of the Flory exponent ν is approximately 0.631, in line with universality arguments, and differs from the usual estimate of 0.588. More generally, the paper provides a powerful new method to study polymer physics. As an example we show that it can be used to describe the approach to entanglement as yet another critical point. This transition is beyond the scope of the standard tube model, a mean field approximation.

The self-consistent field theory (SCF) discussed by de Gennes[1] is a mean field approximation to study melts of flexible polymers. Generalizing this model beyond its mean field roots has obvious advantages. Such a generalization has been attempted[2]. However, while this generalization was appropriate for the intended application, it ignored an important property of polymers. The theory involves a description of polymers in terms of a field $\psi(\vec{r})$, where $\vec{r}$ is the location in physical space of any segment, such that $|\psi(\vec{r})|^2$ is the probability of finding a segment at $\vec{r}$. If the polymer is N segments long, there is no representation in this theory of which segment (1 through N) this field refers to. In other words, reference to the connectivity of the chains is missing. This can be achieved using ideas from functional integration.

The propagator for a single flexible chain may be represented by[3]:

$$G_0(1,2;n) \equiv \langle 1,n| \left[\partial_n - \left(\frac{b^2}{6}\right)\nabla^2\right]^{-1} |2,0\rangle \sim$$
$$\int_{\vec{R}_2}^{\vec{R}_1} \mathcal{D}\vec{R}(n') \exp - \left[\left(\frac{3}{2b^2}\right)\int_0^n dn' \left(\frac{\partial \vec{R}(n')}{\partial n'}\right)^2\right] \tag{1}$$

where b is the bond length of the polymer, and where $\partial_n \equiv \frac{\partial}{\partial n}$. This expression is obtained by considering only the entropy of a flexible chain.

Alternatively, one knows from methods in functional integration that[4]:

$$\langle 1,n| \left[\partial_n - \left(\frac{b^2}{6}\right)\nabla^2\right]^{-1} |2,0\rangle \sim \int \mathcal{D}^2\psi \ \psi^*(\vec{R}_1,n)\psi(\vec{R}_2,0)\exp -[\beta\mathcal{F}]$$
$$\beta\mathcal{F} = \int dn' d^3x \ \psi^*(\vec{x},n') \left[\partial_{n'} - \left(\frac{b^2}{6}\right)\nabla^2\right]\psi(\vec{x},n') \tag{2}$$

where $\mathcal{D}^2\psi \equiv \mathcal{D}\psi^*\mathcal{D}\psi$, $\beta = \frac{1}{k_B T}$, k_B is Boltzmann's constant and T is the temperature. Thus we have another way of thinking about a system of flexible polymers, in terms of $\psi(\vec{x},n)$ and

an energy functional $\beta\mathcal{F}$ which is isomorphic to one that describes diffusion. Here $(\vec{x}, n)$ labels the location $\vec{x}$ in physical space, of the n-th segment of a chain, and $|\psi(\vec{x}, n)|^2$ is the probability of finding a polymer segment at a given location in space, as suggested by Eqn.(15) below. In this sense we have a density functional theory in the style of Kohn and Sham. Kleinert[5] and Semenov et al[6] have proposed similar formalisms. However this paper uses the new formalism to probe the physics of polymer melts in a broader sense.

It is possible to derive from the partition function $\mathcal{Z} = \int \mathcal{D}^2\psi \; \exp{-[\beta\mathcal{F}]}$, a $2p$-point correlation function, which decouples at the non-interacting level into a product of Green's functions for p independent polymers. The main advantage of the functional path integral formalism is that one can now model more easily interactions in systems with large numbers of polymers. The following model, written to look like a Kohn-Sham type density functional theory describes excluded volume effects:

$$H_0 \to H = H_0 + V - \mu$$
$$H_0 \equiv -\left(\frac{b^2}{6}\right)\nabla^2$$
$$V = \frac{v}{2}|\psi(\vec{x}, n)|^2 \tag{3}$$

where v is the usual excluded volume interaction parameter[3], and μ is the chemical potential invoked in the form of a Lagrange multiplier to conserve the number of polymer segments in the system.

The self-avoiding walk of a solitary chain can be modeled by starting from Eqn.(1)[7], by adding to the argument of the exponential on the right hand side, a series of terms which describe the excluded volume interaction between polymer segments. Caution must be used to apply this approach to a system of many polymers.

To understand the physics in the $|\psi|^4$ model, let us extremize the functional density $\mathcal{F}$, while considering only solutions homogeneous in space and in n. This yields a maximum at $\psi = 0$, and minima at:

$$|\psi|^2 = \frac{\mu}{v} \tag{4}$$

This of course leads to an infinity of solutions, equivalent within a phase difference. Following quantum field theory ideas, the phase of the field can be related to scattering, or interaction effects. The physical system can be thought of as localized regions where Eqn.(4) is satisfied, separated by domain walls which permit the transition from one minimum to another.

Note that Eqn.(4) is equivalent to an estimate of the chemical potential $(\mu_0 = c_0 v)$ if the average number density c_0 is known. From this view-point, $c_0 \to 0$ represents a system of polymers which approaches a critical point from *below*. Here we have in mind an analogy with the usual Landau-Ginzburg ϕ^4 model, where the vanishing of the coefficient of the quadratic term in the energy functional leads to a single well potential, signifying a critical point in the phase diagram. This issue was treated by de Gennes by mapping the polymer problem onto one in a zero-component ϕ_j^4 field theory (the self-avoiding walk of a solitary chain)[7]. The different perspective offered by our theory is that the physics of low concentration melts is really an issue in *dynamic* critical phenomena, given the degree of freedom represented by the variable n.

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We can compute a dynamic correction to the free particle Green's function, from the so-called Saturn diagram[8–10]. This diagram is the lowest order non-vanishing $\vec{k}$, ω dependent contribution to the self-energy. To do this calculation, it is first convenient to write $\beta\mathcal{F}$ in a dimensionless form, using $\psi \rightarrow \psi/\sqrt{c_0}$, and scaling all length scales by $c_0^{-1/3}$. This yields $v \rightarrow \alpha = c_0 v$. In the limit of small μ_0,

$$\hat{G}_0(\vec{k},\omega) \rightarrow \left(G_0^{-1}(\vec{k},\omega) - \Sigma(\vec{k},\omega)\right)^{-1}$$

$$\Sigma(\vec{k},\omega) \approx 48\alpha^2 \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k_2}{(2\pi)^3} \frac{1}{-i\omega + (c_0^{-2/3}b^2/6)(\vec{k}_1^2 + \vec{k}_2^2) + (c_0^{-2/3}b^2/6)(\vec{k} - \vec{k}_1 - \vec{k}_2)^2 - 3\mu_0} \quad (5)$$

where $\hat{G}_0(\vec{k},\omega)$ is the Fourier transform of the Green's function introduced in Eqn.(1), and where we have performed the frequency integrations involved in the diagram using the method of residues, and used the mean field value for the chemical potential $\mu_0 = c_0 v \rightarrow 0$. This integral can be found in Hohenberg and Halperin[9] and they use Wilson's renormalization scheme to analyze the properties of this integral. We have been able to evaluate this multi-dimensional integral analytically. The integrals were performed using the identity $1/t = \int_0^\infty d\lambda \exp(-\lambda t)$, and introducing a change of variables to the center-of-mass and relative co-ordinates of $\vec{k}_1, \vec{k}_2$. This allows a separation of variables to occur, permitting an integration over the momentum variables. The final integration is performed using the identity $\int_0^\infty \exp(-Ax)x^k dx = A^{1+k}\Gamma(1 + k)$. In using this identity, we have to perform the integration first in arbitrary dimension d, where the identity is valid, and then continue it formally to $d = 3 - \epsilon$, $\epsilon \rightarrow 0$. The infinities in the integral are then isolated into the Gamma function. As usual, the infinite part is removed by introducing an appropriate counter term in $\beta\mathcal{F}$. This amounts to a renormalization of b. The finite result is:

$$\Sigma(\vec{k},\omega) = \alpha^2 A(2m)^{3-1/C}\left(-i\omega + k^2/(6m) - 3\mu_0\right)^2 \left(C - \ln[2m(-i\omega + k^2/(6m) - 3\mu_0)]\right)$$

$$C = \ln[4\sqrt{3}\pi] + \text{diGamma}(3) \approx 4$$

$$\Sigma(\vec{k},\omega) \approx \alpha^2 AC(2m)^{3-1/C}\left(-i\omega + k^2/(6m) - 3\mu_0\right)^{2-1/C} \quad (6)$$

where $A = 2\sqrt{3}\pi^{-3/2}$, and $m = \frac{3}{c_0^{2/3}b^2}$. The last approximation in Eqn.(6) applies when the argument of the logarithm has a magnitude less than one. Since $\mu_0 \leq 1$, the approximate scaling form thus holds for $|\omega| \leq 1$ and $k \leq \sqrt{18}/b$, with an error of a few percent or less. In writing down these equations, we have implicitly performed *mass* renormalization[9]. The effect of the self-energy Σ is more pronounced at small length scales than it is at long wavelengths. The renormalized Green's function can also be written for $|\vec{k}| \rightarrow 0$ as:

$$\hat{G}(\vec{k},\omega) \approx \frac{1}{-i\omega + \left(\frac{B^2(\omega,\mu_0)}{6}\right)k^2 - \tilde{\mu}(\omega,\mu_0)} \quad (7)$$

where

$$\tilde{\mu}(\omega,\mu_0) = \mu_0 - \alpha^2 A(2m)^{3-1/C}(-i\omega - 3\mu_0)^{2-1/c}$$

$$B^2(\omega,\mu_0) = b^2 c_0^{2/3} + \Delta b^2(\omega,\mu_0)$$

$$\Delta b^2(\omega,\mu_0) = -\alpha^2 (6A)(2m)^{3-1/C}(2 - 1/C)(-i\omega - 3\mu_0)^{1-1/C} \quad (8)$$

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Note that this approximation holds in the regime discussed below Eqn.(6). Now $-i\omega \equiv \partial/\partial n \sim 1/|p-q|$, with p, q referring to the pth and q^{th} segments respectively, while k is the inverse separation in physical space of these segments. In the vicinity of the critical point $\mu_0 = 0$, Δb^2 displays a scaling property viz., $\sim -|p-q|^{-\sigma}$ in the appropriate regime, where we have defined a scaling exponent σ

$$\sigma = (1 - 1/C) \sim 0.75 \tag{9}$$

In this regime, the coefficient of the scaling term behaves as $\sim \alpha^{0.2}$, a weak dependence, if we estimate $v \sim b^3$.

It follows from Eqn.(8) that the effect of the gradient-smoothing term ∇^2 in the energy functional is reduced by an amount $-|\Delta b^2|$, and this effect is dominant for segments separated by a relatively short distance, as it vanishes in the limit of infinite separation. It means that if segments on a chain happen to be in close proximity in the melt, they will tend to stay together due to the reduction of the smoothing term. Neutron scattering experiments or numerical simulations may provide verification of this notion. Neutron experiments are customarily employed in the long wavelength regime to investigate quantities like the radius of gyration of polymeric systems. Other techniques, such as those used by Smith et al[11] may be more useful.

The chain takes on the appearance of pearls on a string which push the ends of the string further away from each other. One way to calculate the scaling properties of the radius of gyration within the current model is to compute vertex corrections within the current model, and then implement Wilson's scaling arguments. However, it is easier to go back to the original theory defined by the energy density $\psi^*(\partial_n + H)\psi$, and truncate it with $\partial_n \to 1/N$ where N is the average chain length of the polymeric system. This is justified on the grounds that we are interested only in long range fluctuations. Accordingly, we also have to restrict the n' integration in $\beta\mathcal{F}$ to a small neighborhood around N. After performing this renormalization, the entire machinery of the static theory of critical phenomena applies. And it follows that very near the critical point $\mu_0 = 0^+$, the correlation length $\xi \equiv R_g \sim N^\nu$, where the lowest order field field theoretic techniques yield $\nu \approx 0.6$, the value obtained by Flory.

More accurate calculations yield[3] a value for ν closer to $0.631^{5,8}$. The standard model for examining the effects of excluded volume interactions yields[12] $\nu \approx 0.588$. The difference between this model and ours was discussed below Eqn.(3).

There is a transition to an entangled state at a value of the concentration $c_0 < 1/v$. To see this let us begin by computing vertex corrections, which can be thought of as giving rise to an effective coupling constant. The lowest order correction comes from the so-called fish diagram with two internal lines. The frequency integral involved in the calculation is performed by closing the contour in the lower half-plane. The remaining momentum integral contains a divergent part which involves an integral from $\sqrt{2m\mu_0}$ to ∞. This is written as an integral from 0 to ∞ minus a finite part from 0 to $\sqrt{2m\mu_0}$. The infinite part is removed in the usual manner with a counter term, and amounts to a renormalization of the coupling constant. This leads to a new coupling constant α_R:

$$\alpha_R(q) = \alpha - \alpha^2 \tilde{\Gamma}(q)$$
$$\tilde{\Gamma}(q) \approx \left(\frac{(6\mu_0)^{3/2}}{24\pi^2 c_0 b^3} \right) \frac{1}{-i\omega_q - 2\mu_0 + \vec{q}^2/2m} + \mathcal{O}(\vec{q}^2) \tag{10}$$

where $q \equiv (\vec{q}, \omega_q)$, etc. and $\mu_0 << 1$. Notice that to this order in perturbation theory, an increasing concentration signified by an increasing α leads to a lower effective coupling constant, consistent with the latter half of Flory's theorem. We can define a beta function as is done conventionally in Renormalization Group theory, viz.,

$$\beta(\hat{\alpha}_R) = \frac{\partial \hat{\alpha}_R}{\partial \ln y} \approx -\hat{\alpha}_R + \hat{\alpha}_R^2$$

$$y = -i\omega_q - 2\mu_0 \equiv 1/N - 2\mu_0$$

$$\hat{\alpha}_R \equiv \left(\frac{(6\mu_0)^{3/2}}{24\pi^2 c_0 b^3} \right) \alpha_R(\vec{q} = 0) \tag{11}$$

where y plays the role of a scaling parameter, and as $y \to 0$ ($N \to (2\mu_0)^{-1}$), we see that $\hat{\alpha}_R$ flows towards a nontrivial fixed point viz., $\hat{\alpha}_R = 1$. As an example, it can be checked in the case of polydimethylsiloxane (PDMS), that $c_0 \sim 3 \times 10^{-3}$ cm^{-3}, $b \sim 1.5 \mathring{A}$, yielding $N_c \sim 167$, which is close to the experimentally determined[13] critical entanglement chain length of ~ 200. Similarly, for polystyrene, using $b \sim 1 \mathring{A}$, we get $N_c \sim 320$, reasonably close to the critical chain length estimated by the viscosity measurements of Onogi et al[14]. To the lowest order, the structure factor $\hat{S}(q) = (2/3)\tilde{\Gamma}(q)$. It diverges as $|\vec{q}|^{-2}$ at $y = 0$, analogous to the behavior at a critical point. The Young's modulus Y of the system is given by[15] $Y \propto \hat{S}(\vec{q} = 0, \omega)$, and it will show a dramatic rise as the chain length N is increased towards N_c for $\mu_0 \neq 0$. For these reasons we can identify this critical point with the onset of entanglement. Note that the approximation to $\hat{S}(q)$ we have used here will not work past the transition to entanglement. There is some indication of fluctuating behavior near the entanglement transition in the classic viscoelasticity measurements of Onogi et al[14], as indicated by earlier phenomenological analyses[15,16].

Fluctuations in the system tend to decrease as c_0 increases away from the critical point just discussed. So for finite concentrations we expect mean field theory to hold. In this limit, we get a time-dependent Landau-Ginzburg equation (time $\equiv n$), by extremizing $\beta\mathcal{F}$ with respect to ψ^*:

$$\left[\frac{\partial}{\partial n} - \left(\frac{b^2}{6} \right) \nabla^2 - \mu_0 + v|\psi(\vec{x}, n)|^2 \right] \psi(\vec{x}, n) = 0 \tag{12}$$

For the moment, let us suppose that there is no n dependence in ψ. Then the model reduces to the SCF equation. Noting the similarity of this equation to the one used to describe bosonic fluids[17], we seek tube-like solutions in cylindrical geometry, viz., $\psi(\rho, \phi) = \exp(is\phi)f(\rho)$, s is an integer:

$$\frac{1}{\rho} \frac{d}{d\rho} \left(\rho \frac{df(\rho)}{d\rho} \right) + \left(1 - \frac{s^2}{\rho^2} \right) f(\rho) - f^3(\rho) = 0 \tag{13}$$

where ρ has been made dimensionless by the length scale

$$a = b/\sqrt{6c_0 v} \tag{14}$$

We see that for $\rho \to 0$, assuming $|f(\rho)| \to 0$, we get a solution proportional to $J_s(\rho) \sim \rho^{s}$[17]. By choosing the amplitude of this solution correctly, one can match it for large ρ to

a constant solution $f(\rho) = \pm\sqrt{1 - s^2/\rho^2}$ (see Fig.(1)). This solution may also be continued mathematically to $s \to 0$. But then the $s = 0$ solution has an infinite slope at the origin. The radial extent of these solutions is $\sim s\,a$, for $s \neq 0$. From excluded volume considerations, the maximum density possible in the system is $1/v$, and for densities approaching $1/v$, $a \sim b/\sqrt{6}$. Physically, these solutions are reminiscent of the tube model of Edwards[3]. They indicate that the tubes are not empty, but have a concentration of polymers given by $[f(\rho)]^2$. It may be possible to use numerical simulations to check if the qualitative features of the occupation profile $[f(\rho)]^2$ can be reproduced[18].

As discussed by Fetter, the higher the value of s, the higher the energy of the tube-like configuration, and the system will prefer to have many tubes with a low s than a few with a large s. We have thus derived from our theory a tube model with a tube radius a, which is exceedingly large for small densities, and asymptotes smoothly in an inverse square root fashion to $\sim b/\sqrt{6}$ as the density approaches $1/v$. Since the monomer length b is of the order of a few Angstroms, the magnitude of the tube radius for $c_0 v \sim 10^{-2}$ is a few monomer lengths. This is in qualitative agreement with estimates which can be found in the literature[3].

In the theory of superfluids[17], these cylindrical structures are viewed as idealizations of vortices, caused by the rotation of the fluid. In our case we can derive an equation of continuity from Eqn.(12):

$$\frac{\partial |\psi|^2}{\partial n} = -\vec{\nabla} \cdot \vec{j} + S$$

$$\vec{j} = \left(\frac{b^2}{6}\right)\left(\psi^*\vec{\nabla}\psi + c.c.\right)$$

$$S = \left(\frac{b^2}{3}\right)|\vec{\nabla}\psi|^2 + 2\mu_0|\psi|^2 - v|\psi|^4 \tag{15}$$

It follows by examining the current $\vec{j}$, that the tube-like solutions are not caused by rotation, but rather, there is a *radial velocity* due to the ρ dependence of the solution. There is yet another solution to Eqn.(12), and is obtained by assuming that it is dependent solely on n, which yields $\psi(n) = [1 + \exp(-2n\alpha)]^{-1/2}$. More general solutions can undoubtedly be found numerically by studying Eqn.(12) with various boundary conditions.

We speculate that the phase of the field ψ may be useful in quantifying the notion of entanglement in polymers. Ultimately the theory needs to be generalized to handle polymer dynamics.

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FIG. 1. Numerical solutions of Eqn.(13) for s=1 and s=2. Both curves asymptote to unity, but on different scales.